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Analysis of Organophosphorus Pesticide Samples by High-Performance Liquid Chromatography/Mass Spectrometry and High-Performance Liquid Chromatography/Mass Spectrometry/Mass Spectrometry

(U.S.) Environmental Monitoring Systems Lab., Las Vegas, NV

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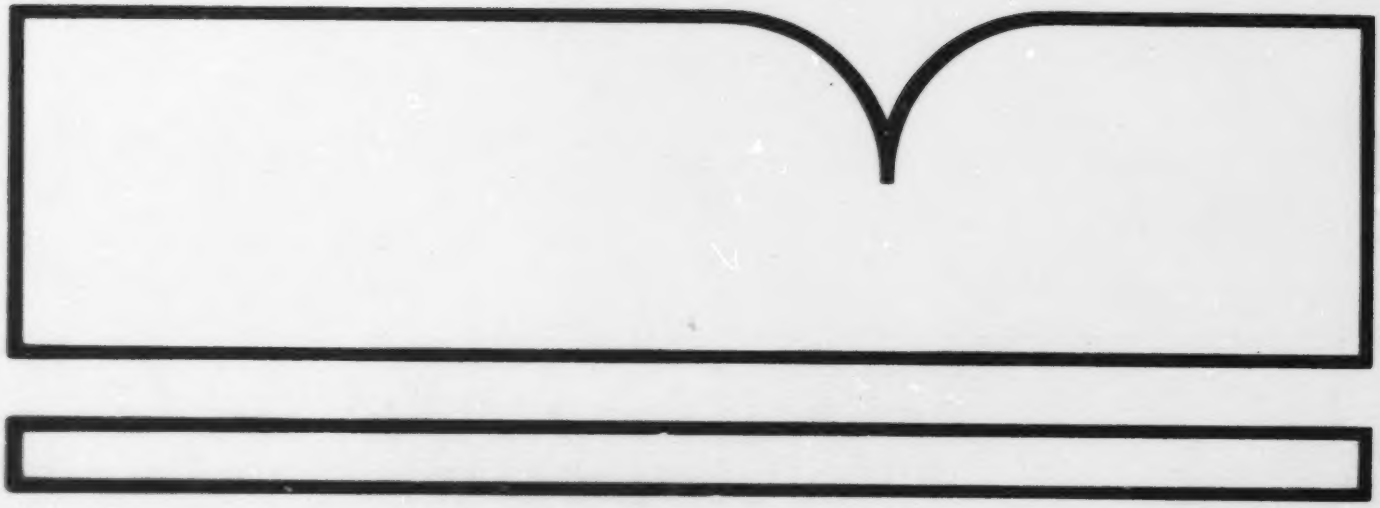

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16. ABSTRACT

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Analysis of Organophosphorus Pesticide Samples by High-Performance Liquid Chromatography/Mass Spectrometry and High-Performance Liquid Chromatography/Mass Spectrometry/Mass Spectrometry

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■ Ten analytes from the U.S. Environmental Protection Agency's SW-846 Method 8140, Organophosphorus Pesticide Parameters, were subjected to analysis by high-performance liquid chromatography/mass spectrometry (HPLC/MS) and HPLC/MS/MS with thermospray ionization. The compounds chosen suffered poor recoveries under analysis by method 8140, which is a gas chromatographic procedure. Limits of detection, precision values, and retention times were generated with HPLC/MS methods on pure analytical standards. Collision activated dissociation daughter ion spectra were also collected by tandem mass spectrometric techniques. Four environmental samples known to contain organophosphorus pesticides were analyzed by HPLC/MS, and these results were compared with similar analyses by GC/MS. Tandem mass spectrometry was used to confirm the compounds identified by HPLC/MS.

Introduction

The U.S. Environmental Protection Agency recently conducted a single laboratory validation of SW-846 Method 8140, Organophosphorus Pesticide Parameters (*1*). This procedure is a gas chromatographic (GC) method for the analysis of organophosphorus pesticides in water, soil, and hazardous waste. In addition to the presentation of data on precision and accuracy, the validation report (*1*) provided findings on analytical difficulties encountered with specific organophosphorus pesticides. The purpose of this present work is to investigate the use of high-performance liquid chromatography/mass spectrometry (HPLC/MS) and high-performance liquid chromatography/mass spectrometry/mass spectrometry (HPLC/MS/MS) for the analysis of these problem compounds.

Recent studies of organophosphates have included tandem mass spectrometry with packed column or solid probe introduction (*2*), positive and negative ion chemical ionization with direct liquid introduction (DLI)(*3*), and thermospray mass spectrometry (*4*). The work described in this paper further explores the use of thermospray ionization combined with tandem mass spectrometry to study problem organophosphorus pesticides. As a result of thermal lability or other degradation pathways, these pesticides have been difficult to study by GC. Earlier studies on organophosphorus pesticides by mass spectrometry had utilized electron impact (EI)(*5*), positive ion chemical ionization (CI)(*6*, *7*), and electron capture CI (*8–10*).

Thermospray mass spectrometry (*11*) has been widely used in recent years for the analysis of a variety of compounds. Since one of the ionization mechanisms for thermospray introduction is similar to ammonia chemical ionization (*12*), compounds with proton affinities greater than ammonia are readily protonated in this technique. Although the proton affinities for the organophosphorus pesticides have not been measured, these compounds are expected to show gas-phase basicities greater than ammonia (*13*). The usefulness of tandem mass spectrometry in conjunction with thermospray ionization has been shown (*14*). The only ions produced under thermospray ionization are often the protonated species or the ammonium adduct ion or both. When this is the case, collisionally activated dissociation (CAD) experiments in the tandem mass spectrometer on the ions of interest provide structural information that is otherwise unobtainable.

The use of HPLC methods with mass spectrometry provides the analyst with an alternative to GC/MS. Because of low volatility, thermal lability, or polarity, many compounds do not pass through a GC intact or do not chromatograph well. The chromatographic separation of the HPLC system enables the on-line analyses of samples for target compounds. In addition, this separation provides the necessary cleanup for dirty samples before analysis by tandem mass spectrometry. By utilizing the chromatographic column, two levels of separation are provided with thermospray MS/MS: chromatographic separation and electronic separation in the first quadrupole analyzer. Combined with the selective nature of the thermospray process (filament off), this technique provides a powerful tool for monitoring target compounds in complex samples.

Experimental Section

Materials. Organophosphorus pesticide standards were obtained through the Pesticide and Industrial Chemicals Repository, U.S. Environmental Protection Agency, Las Vegas, NV.

Sample Preparation. Four environmental soil samples were received from a U.S. EPA regional laboratory for experimental use. A microextraction was performed on each sample. A disposable pipet was packed with glass wool and anhydrous Na_2SO_4 and then moistened with methylene chloride. Approximately 1 g of each sample was weighed out; two of the samples were very moist, and these were mixed with an equivalent amount of Na_2SO_4 and packed into the pipet. Approximately 4 mL of methylene chloride followed by ~4 mL of methanol was used to extract the sample. Because of the high levels of pentachloronitrobenzene, one of the sample extracts was blown down with nitrogen to ~1 mL and enough methylene chloride was added to give a total volume of 4 mL. The other extracts were also adjusted (nitrogen blow down) initially to 4 mL.

Liquid Chromatography/Mass Spectrometry. The liquid chromatography/mass spectrometry system has been described previously (*15*). Briefly, a Finnigan MAT TSQ 45 was used with a Vestec Thermospray interface. A flow of 0.4 mL/min was used through a 10 cm × 2 mm ODS Hypersil 5-μm PN-Special analytical column from Keystone Scientific Inc. (State College, PA). A Spectra-Physics SP8700XR pump was programmed to deliver the following composition of the mobile phase by using a linear gradient:

time, min	H_2O, %	CH_3OH, %	CH_2Cl_2, %
0	58	40	2
12	0	98	2
17	0	98	2

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Table I. Organophosphorus Pesticides

compound	MW	formula
disulfoton	274	$(C_2H_5O)_2P(S)SC_2H_4SC_2H_5$
trichlorfon	256	$Cl_3CCH_2OP(O)(OCH_3)_2$
fensulfothion	308	$(C_2H_5O)_2P(S)OC_6H_4S(O)CH_3$
methyl parathion	263	$(CH_3O)_2P(S)OC_6H_4NO_2$
monocrotophos	223	$(CH_3O)_2P(O)OC(CH_3)CHC(O)NHCH_3$
naled	378	$Cl_2BrCCHBrOP(O)(OCH_3)_2$
merphos	298	$P(SC_4H_9)_3$
dichlorvos	220	$Cl_2CCHOP(O)(OCH_3)_2$
phorate	260	$(C_2H_5O)_2P(S)SCH_2SC_2H_5$
dimethoate	229	$(CH_3O)_2P(S)SCH_2C(O)NHCH_3$

An Isco LC-5000 syringe pump was used to deliver a flow of 0.88 mL/min 0.1 M ammonium acetate postcolumn and before the thermospray interface. A Lee Visco mixer (Lee Co., Westbrook, CT) was used to connect the syringe pump to the rest of the chromatographic system. A 10-μL sample loop was used on the injector for all analyses.

Typical operating temperatures of the thermospray interface were as follows: T (vaporizer) = 124–130 °C; T (tip) = 214–228 °C; T (source) = 270–275 °C; T (jet) = 210–220 °C.

The CAD experiments were conducted at a collision energy at 20 eV with argon at a pressure of 1 mTorr unless otherwise noted.

Single quadrupole scans were typically taken from masses 150 to 450 in 1.5 s.

Results and Discussion

The organophosphorus pesticides that were investigated in this study are listed in Table I with their molecular weights and chemical formulas. Each compound was selected according to the difficulty posed when analyzed by the U.S. Environmental Protection Agency's SW-846 method 8140 (*1*). Trichlorfon rearranges and is dehydrochlorinated in acidic, neutral, or basic media to form dichlorvos and hydrochloric acid. Methyl parathion is a thermally labile and chemically reactive compound that decomposes during sample preparation and analysis. Naled is converted to dichlorvos on column by a debromination reaction; this reaction may also occur during sample workup. Merphos is readily oxidized to the phosphine oxide in the environment and during storage (*16*). Recoveries of dichlorvos are low and variable because of its volatility and relatively high aqueous solubility. The other compounds show poor to fair recoveries with method 8140 in at least one of the extraction procedures tested in the single laboratory validation study (*1*).

A two-pronged approach was taken for the current work. First, standards of the 10 compounds listed in Table I were injected into the analytical system with the retention time and the single quadrupole spectrum recorded for each analyte. CAD experiments were run on the same compounds, and these spectra were tabulated. Limits of detection, calibration curves, and precision data were taken by using these standard compounds. The second step was to analyze four environmental soil samples that were known (as reported by GC/MS) to contain several of the pesticides listed in Table I.

Table II lists the retention times (achieved by using the LC program listed in the Experimental Section) and the major ions (>5%) present in the thermospray single quadrupole spectra of the ten organophosphorus pesticides of interest. In most cases the $(M + H)^+$ and $(M + NH_4)^+$ adduct ions are the only ions of significant abundance. The mass spectra of four of the compounds show additional peaks. Ions at m/z 234 and 251 for methyl parathion coelute with the $(M + H)^+$ and $(M + NH_4)^+$ ions at

Table II. Retention Times and Thermospray Mass Spectra of Organophosphorus Pesticides

compound	RT, min	mass spectra (% rel abund)[a]
monocrotophos	1:09	241 (100), 224 (14)
trichlorfon	1:22	274 (100), 257 (19), 238 (19)
dimethoate	1:28	247 (20), 230 (100)
dichlorvos	4:40	238 (100), 221 (40)
naled	9:16	398 (100), 381 (23), 238 (5), 221 (2)
fensulfothion	9:52	326 (10), 309 (100)
methyl parathion	10:52	281 (100), 264 (8), 251 (21), 234 (48)
phorate	13:30	278 (4), 261 (100)
disulfoton	13:55	292 (10), 275 (100)
merphos	18:51	315 (100), 299 (15)

[a] For molecules containing Cl, Br, and S, only the base peak of the isotopic cluster is listed.

m/z 264 and 281, respectively. Since this compound has been reported to be thermally labile and chemically reactive, these ions possibly represent decomposition or reduction products that occur during mass spectral analysis. Yinon (*17*) has reported that $(M + H - 30)^+$ ions in the chemical ionization (CI) mass spectra of nitroaromatic compounds can be due to reduction of the nitro group to the corresponding amine, a process found to occur in a CI source. These ions could also arise from loss of NO• from both the $(M + H)^+$ and $(M + NH_4)^+$ ions due to the thermospray ionization fragmentation. This is a common loss in electron ionization especially with an electron-donating group para to the nitro group (*18*). The loss of NO• from nitroaromatic compounds under "soft" ionization conditions (e.g., fast atom bombardonment) has also been reported (*19*).

In addition to the expected $(M + H)^+$ and $(M + NH_4)^+$ ions, the thermospray mass spectrum of trichlorfon includes a m/z 238 peak which is presumably due to the $(M + NH_4)^+$ ion of dichlorvos. Since trichlorfon is known to rearrange and lose hydrogen chloride to form dichlorvos, this reaction appears to occur also during the thermospray process.

Naled shows small signs of undergoing debromination to form dichlorvos as indicated by the m/z 221 and 238 ions, which are the ions generated when dichlorvos is injected into the system and represent the $(M + H)^+$ and the $(M + NH_4)^+$ ions, respectively, of dichlorvos. Since these ions show 2 and 5% relative abundance, respectively, they do not represent a major channel of reaction on HPLC/MS. These ion coelute with the m/z 381 and 398 ions that represent the $(M + H)^+$ and $(M + NH_4)^+$ ions, respectively, of naled. Thus, the debromination is occurring upon introduction into the mass spectrometer.

Merphos shows a large contamination of merphos oxide, $(n\text{-}C_4H_9S)_3P{=}O$, as indicated by its protonated molecule, the m/z 315 ion listed in Table II. The major portion of this species eluted ~2.5 min before the merphos peak on the HPLC column. This indicates that the merphos standard was contaminated with the oxide, which is consistent with reports of degradation of this compound on storage. However, approximately 5–10% of the m/z 315 ion intensity reported in Table II was due to an ion that coeluted with merphos. Presumably, further degradation of the standard is associated with introduction into the mass spectrometer. None of the other standard compounds showed any signs of degradation during introduction into the analytical system.

Table III shows the major ions (>3% relative abundance) from the CAD spectra of the organophosphorus compounds listed in Table I. These experiments were performed by selecting the $(M + H)^+$ ion [or $(M + NH_4)^+$]

Table III. CAD Daughter Ions from Organophosphorus Pesticides Introduced via Thermospray Ionization

compound	parent ion	daughter ions (% rel abund)
monocrotophos	241	193 (6), 127 (100), 109 (8), 98 (40), 67 (12), 58 (37)
trichlorfon	274	257 (5), 221 (8), 141 (3), 127 (22), 109 (100), 108 (3), 93 (2), 83 (4), 79 (11)
dimethoate	230	199 (5), 171 (15), 157 (22), 143 (11), 125 (100), 93 (3), 88 (20), 79 (10), 47 (5), 42 (8)
dichlorvos	221	221 (3), 141 (12), 127 (18), 109 (100), 108 (4), 97 (3), 95 (3), 79 (13), 47 (3)
	238	221 (13), 145 (3), 141 (2), 127 (18), 109 (100), 108 (4), 97 (3), 95 (2), 79 (9)
naled	381	302 (4), 255 (7), 173 (6), 145 (12), 127 (100), 126 (4), 109 (27)
fensulfothion	309	309 (3), 281 (11), 267 (5), 253 (33), 237 (7), 235 (77), 219 (26), 218 (3), 173 (83), 157 (100), 156 (15), 142 (4), 140 (18), 125 (4), 110 (4), 94 (5)
methyl parathion	281	281 (8), 264 (22), 232 (50), 200 (4), 194 (5), 186 (6), 154 (6), 125 (100), 123 (15), 109 (25), 89 (4), 79 (11), 75 (4), 45 (8)
phorate	261	199 (3), 171 (3), 153 (2), 143 (3), 75 (100), 47 (3)
disulfoton	275	89 (100), 61 (3) (10 eV)
merphos	299	197 (3), 153 (75), 152 (8), 134 (4), 131 (7), 97 (47), 91 (12), 63 (4), 57 (100), 55 (6), 41 (8)
merphos oxide	315	169 (38), 168 (4), 151 (5), 113 (35), 112 (5), 91 (15), 89 (8), 57 (100), 41 (8)

in quadrupole 1 and scanning quadrupole 3 to examine the daughter ions that result from the collisions that take place in quadrupole 2, at an energy of 20 eV and argon pressure of 1 mTorr. While most of the ion current remains in the pseudomolecular ions (protonated molecule or ammonium adduct ion) upon thermospray introduction, these CAD spectra show ions characteristic of the structure of the molecule or class of compound. For example, for the phosphorothionates or the phosphorodithioates, the *O,O*-dimethyl compounds (methyl parathion and dimethoate) show a strong m/z 125 ion which can be attributed to the $(CH_3O)_2P{=}S^+$ ion or, upon thermal rearrangement, to the $(CH_3S)(CH_3O)P{=}O^+$ ion. These are characteristic ions formed under electron impact mass spectrometry conditions (*20*). For two of the compounds listed in Table III, the CAD spectra give limited but specific information. The spectra for the phosphordithioates, disulfoton and phorate, show only one ion greater than 3% relative abundance. The ion in both cases is of the form $C_nH_{2n}SC_2H_5^+$ which appears at m/z 89 for disulfoton and m/z 75 for phorate.

The CAD spectra of the $(M + NH_4)^+$ ions are given exclusively for trichlorfon, methyl parathion, and monocrotophos, because these were the major ions in the single quadrupole thermospray spectra. The CAD spectra of both the $(M + H)^+$ and the $(M + NH_4)^+$ ions are given for dichlorvos. The spectra are identical for ions with greater than 10% relative abundance except for m/z 221 and 141. This similarity is typical for the CAD spectra of these two ions; they should be expected to give similar structural information.

The CAD spectrum for the m/z 315 from the oxide of merphos is given for comparison with the corresponding ion from merphos. These are similar except for the m/z 169 and 113 ions from merphos oxide and the m/z 153 and 97 ions from merphos. These ions are similar except for the addition of oxygen for the species from merphos oxide.

A useful comparison can be made betweeen the data in Table III and data from a recent paper by Hummel and Yost (*2*). In this work, CAD spectra were generated for six of the compounds listed in Table I. The CAD conditions were the same except that nitrogen was used as the collision gas. The samples were introduced by solid probe or by packed column GC and methane chemical ionization was used to ionize the compounds in the previous study. The comparison shows the spectra are similar qualitatively, but the previous work shows a skewing toward the higher masses in these daughter ion spectra. For example, in the earlier work three of the six spectra show the $(M + H)^+$ or parent ion as the base peak, while in the present work most of the parent ions showed a relative intensity 3% or less. One explanation for this phenomenon is that the use of argon, instead of nitrogen, results in a 35% increase in the center of mass energy (*21*). Consequently, more fragmentation of the parent ion occurs in the present study. The only other discrepancy is the difference between the monocrotophos spectra; m/z 96 is the base peak in the previous study while an ion at m/z 98 is present at 40% in the current work.

A similar comparison can be made with the data of Roach and Andrzejewski (*22*) in which a triple quadrupole mass spectrometer equipped with a direct exposure probe was used to look at disulfoton, dimethoate, and methyl parathion among other compounds. Methane chemical ionization was used to generate $(M + H)^+$ ions for these compounds. The CAD conditions were as follows: 1.8 mTorr of argon; −15 eV collision energy. The direct exposure probe was heated at a rate of 20 mA/s during sample introduction. The CAD spectra of the disulfoton, dimethoate, and methyl parathion are qualitatively similar to the current work. The m/z 89 ion remains the only peak above 5% in disulfoton. For dimethoate the m/z 171 and 199 ions are of higher relative abundance than in the present study. For methyl parathion the base peak is the m/z 109 ion in the previous work, while the m/z 125 ion is the most intense peak in this work. Since the sample introduction mode was different (direct exposure probe versus thermospray ionization), the thermal rearrangement described in a previous work (*20*) for dimethoxy phosphorothionates may be more predominant. That rearrangement ion can show a facile loss of SR$^\bullet$ (R = $C_6H_4NO_2$ for methyl parathion) to yield $(CH_3O)_2P{=}O^+$.

Limits of Detection. The limits of detection (LOD) were determined for eight of the compounds investigated. LOD is defined as the lowest concentration of an analyte that an analytical process can detect and is located at 3σ (σ = standard deviation) above the gross blank signal (*23*). The data set, consisting of three replicates of four standard concentration levels and solvent blanks, is summarized in Table IV. This table shows the precision for three replicate injections of standard compounds, in addition to the LOD in total amount injected. These LODs, which were achieved with the single quadrupole full scanning mode, compare favorably with the single reaction monitoring LODs reported by Hummel and Yost (*2*). The number calculated for merphos is in doubt, because a large proportion of this compound had been oxidized.

Environmental Sample Analysis. Four samples obtained from a U.S. Environmental Protection Agency regional laboratory, and known (by GC/MS analysis) to contain organophosphorus pesticides, were analyzed for the compounds listed in Table I. These samples were injected and eluted with the same mobile-phase gradient

Table IV. Precision and Limits of Detection for Organophosphorus Pesticide Standards

compound	quantn ion	standard amt, ng	RSD, %	LOD, ng
dimethoate	230	20	2.2	
		125	4.2	
		250	13	
		500	7.3	2
dichlorvos	238	20	16	
		125	13	
		250	5.7	
		500	4.2	
				4
naled	398	20	9.5	
		125	9.6	
		250	5.2	
		500	6.3	
				0.2
fensulfothion	309	20	4.1	
		125	9.2	
		250	9.8	
		500	2.5	
				0.4
methyl parathion	281	20		
		125	7.1	
		250	4.8	
		500	1.5	
				30
phorate	261	20	0.84	
		125	14	
		250	7.1	
		500	4.0	
				2
disulfoton	275	20	2.2	
		125	14	
		250	6.7	
		500	3.0	
				1
merphos	299	20	5.5	
		125	17	
		250	3.9	
		500	5.3	
				1

that was used for the standards. The retention times plus the CAD spectra of both the sample and the standard were used to confirm the identities of the pesticides. Since these were real samples, many other compounds besides those of interest were present. For sorting out interferences, the CAD daughter ion spectra proved invaluable. For example, Figure 1 shows the total reconstructed chromatogram plus the mass chromatogram for m/z 275. At least two compounds give rise to peaks at m/z 275 in the retention time region of disulfoton. Figure 2 represents the total reconstructed chromatogram plus the mass chromatograms for three ions eluting in the retention time region for disulfoton for the experiment in which m/z 275 was focused in the first quadrupole, while the third quadrupole was scanned from m/z 30 to 350. The second quadrupole was pressurized with argon. As can be seen, responses from two compounds occur under these conditions. The CAD daughter ion spectrum identifies the second of these compounds as disulfoton because of the intense m/z 89 peak. Table III indicates that the m/z 89 ion is the base peak in the CAD spectrum of disulfoton. The CAD spectrum of the first compound eluting in the chromatogram (Figure 2) showed the m/z 229 peak as the major daughter ion. Only by using the MS/MS capabilities of the instrument was the m/z 275 ion able to be resolved and disulfoton identified.

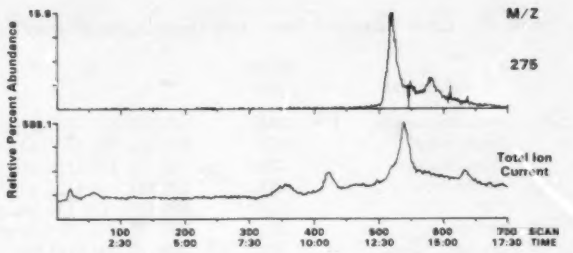

Figure 1. HPLC/MS total and mass chromatograms of soil sample extract containing disulfoton.

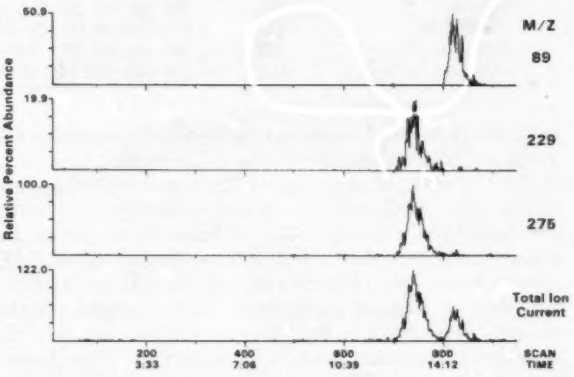

Figure 2. HPLC/MS/MS total and mass chromatograms of soil sample extract containing disulfoton.

The results of the analyses of the four pesticide samples are summarized in Table V. Quantitative analyses were performed only for those compounds listed in Table I. Ethyl parathion was identified and was present in large amounts in most of the samples but was not quantified. The compounds that were quantified were related to the intensity of the $(M + H)^+$ ion or the $(M + NH_4)^+$ ion (for

Table V. Concentration of Organophosphorus Pesticides Found in Environmental Samples

sample	compound	quantn ion	amt calcd, mg/kg LC/MS	amt calcd, mg/kg GC/MS	LC/MS LOD,[c] mg/kg	GC/MS LOQ,[d] mg/kg
1	disulfoton	275	4.41	0.750 *J*[a]	0.24	1.3
	methyl parathion	281	ND[b]	1.10 *J*[a]	7.1	2.0
	phorate	261	4.80	ND[b]	0.47	1.3
2	dimethoate	230	1740	144	0.82	9.4
	phorate	261	66.9	54.3	0.82	3.4
	disulfoton	89	26.8	4.85	0.41	3.4
	methyl parathion	281	28500	28700	12	5.4
3	disulfoton	275	98.8	110	0.79	9.3
	phorate	261	44.7	19.0	1.6	9.3
4	disulfoton	89	45.0	130	0.51	2.5
	methyl parathion	281	115	150	15	4.5

[a] *J* value indicates detected but under limit of quantitation (LOQ). [b] Not detected. [c] Limit of detection. [d] Limit of quantitation.

methyl parathion) in the 12.5 ng/μL standard. The standards for these compounds showed a linearity of response over the concentration levels listed in Table IV of at least 0.999 (correlation coefficient). The CAD daughter ion at m/z 89 was used as the quantitation ion for disulfoton in samples 2 and 4 because of an interfering peak at m/z 275 (vide supra). The amounts for dimethoate and methyl parathion in sample 2 were calculated on the basis of the analysis of a diluted sample (1:100) and a 25 ng/μL standard. The results from the GC/MS analyses are given for reference. Qualitatively, the results show good agreement. Only in sample 1 is there some doubt about the presence of compounds. Methyl parathion was flagged as being present by the GC/MS analysis but at lower than the limit of quantitation by this technique. This compound was not identified by LC/MS; the level reported by GC/MS was below the LC/MS LOD. Phorate in sample 1 is identified by the LC/MS analysis but not by GC/MS techniques. The same compounds were detected by both techniques in the rest of the samples. In some cases the results are quantitatively very close, as for phorate and methyl parathion in sample 2 and disulfoton in sample 3. The amounts calculated for dimethoate and phorate are higher under LC/MS analysis for all occurrences of these compounds. Since these compounds have shown difficulties under GC analysis, it is possible that some of these compounds were degraded or irreversibly absorbed on the GC.

Conclusion

HPLC/MS and HPLC/MS/MS have proven useful for the determination of organophosphorus pesticides. Since these compounds are quite basic, the limits of detection under thermospray ionization are good and generally better than those attained under GC/MS. The precision of thermospray/MS, as summarized in Table IV, is generally better than 10% relative standard deviation for standard compounds with an external standard method. Some of the problems with these organophosphorus pesticides that were identified with GC analysis remain a problem with HPLC/MS. Merphos degrades on storage to its oxide; consequently, this compound will still present problems for the analyst. Likewise, trichlorfon shows approximately a 16% conversion to dichlorvos under thermospray introduction. Other compounds appear to be relatively stable to HPLC/MS analysis. The degradation of naled to dichlorvos under GC conditions appears not to be a problem with thermospray introduction.

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Registry No. Disulfoton, 298-04-4; trichlorfon, 52-68-6; fensulfothion, 115-90-2; methyl parathion, 298-00-0; monocrotophos, 6923-22-4; naled, 300-76-5; merphos, 150-50-5; dichlorvos, 62-73-7; phorate, 298-02-2; dimethoate, 60-51-5.

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